# Supporting Information

## Designing Fluorine-free Electrolytes for Stable Sodium Metal Anodes and High-Power Seawater Batteries via SEI Reconstruction

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#### 1. Experimental Section/Methods

*Electrolyte preparation:* NaClO<sub>4</sub> (98%), NaBH<sub>4</sub> (99.99%), diethylene glycol dimethyl ether (DEGDME, 99.5% anhydrous), tetraethylene glycol dimethyl ether (TEGDME, 99%) were purchased from Sigma-Aldrich. NaOTf (>98%) and EC/PC (1:1 volume ratio) + 5 wt% FEC solvents were purchased from Tokyo Chemical Industry (TCI) and PANAX E-TEC., Korea, respectively. Sodium salts and electrolyte solvents, except TEGDME, were stored in an Arfilled glove box to prevent O<sub>2</sub> and H<sub>2</sub>O contamination. TEGDME was purified by distillation, by using CaH<sub>2</sub> to get rid of H<sub>2</sub>O impurities. Sodium salts were dried overnight in a vacuum oven at 110 °C. After drying, salts were transferred to the glovebox antechamber immediately to minimize air exposure, followed by vacuum drying for over 1 hour. All electrolytes were prepared to 1 M concentration.

Galvanostatic cycling tests: Galvanostatic cycling tests were conducted to fabricate coin-type cells (CR-2032). Sodium metal (cubes, contains mineral oil, 99.9%) was purchased from Sigma-Aldrich. The sodium cube was carefully wiped out to remove mineral oil on the surface, followed by slicing every side of the cube to expose the shiny, metallic sodium. Then, sodium was placed inside of the poly glove and pressed by a vial to make flat, approximately 100  $\mu$ m of sodium foil. Galvanostatic tests of Na||Na symmetric cell were conducted by using 11  $\Phi$  sodium electrodes, 30  $\mu$ l of each electrolyte, and celgard 2400 separator (Welcos Ltd.), except the coin cell fabricated by applying 1M NaClO<sub>4</sub> EC/PC + 5 wt% FEC. In this case, 70  $\mu$ l of electrolyte was consumed to wet the glass fiber (GFF) separator (Whatman) sufficiently. For modified Aurbach's measurements, sodium metal was plated 5 mA h cm<sup>-2</sup> with a current density of 1 mA cm<sup>-2</sup>. Thereafter, 9 cycles were performed under conditions of 1 mA cm<sup>-2</sup> and 1 mAh cm<sup>-2</sup>, and finally, the electrochemically active sodium was

completely removed with a cut-off voltage of 1 V. For artificial coating of NaH and NaBO<sub>2</sub>, 100 mg of each powder was dispersed in 5 ml of DEGDME. Then, 15  $\mu$ L of dispersion was dropped on sodium electrodes, followed by vacuum drying in the glovebox antechamber. For full-cell tests, Na<sub>0.83</sub>Fe<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> cathode was synthesized according to the previous report<sup>1</sup>. It was coated on Al/C current collector with mass ratio of 8: 1: 1 (active material: conductive carbon: PVDF) and mass loading was approximately 3.5 mg cm<sup>-2</sup>. Na||Na<sub>0.83</sub>Fe<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> full-cells were operated at 1.5 – 4.3V with 1M NaClO<sub>4</sub> EC/PC + 5 wt% FEC electrolyte under 1C-rate (180 mA g<sup>-1</sup>).

*EIS tests*: EIS tests were performed at potentiostat (Biologics) under the same conditions as the Na||Na symmetric cell prepared for the galvanostatic tests. The cell was directly cycled at the potentiostat, and the EIS tests were conducted every 20 cycles until 100 cycles. The rest period between galvanostatic cycling and EIS tests was 5 minutes. During EIS tests, a sine wave with an amplitude of 10 mV from 10 mHz to 100 kHz was applied.

*Online Electrochemical Mass Spectrometry (OEMS):* Gas-evolution profiles of Na||Cu half cells were measured by home-built OEMS. Hermetically sealed cells (Tomcell<sup>®</sup>) were assembled in the Ar-filled glovebox with the metallic Na electrode (diameter: 12 mm), two pieces of separators (Celgard<sup>®</sup> 2500 and Whatman GF/C), mesh-type Cu electrode (diameter: 12 mm), and 200 µL of TEGDME containing 1.0 M NaBH<sub>4</sub> as the electrolyte solution. The assembled cell was connected to the OEMS analyzer and rested for 7~8 h prior to the cell operation. The cell was initially charged with a charge capacity of 2 mA h cm<sup>-2</sup>, followed by cycling at a capacity of 1 mA h cm<sup>-2</sup> and a current density of 0.5 mA cm<sup>-2</sup>. Electrochemical measurements were carried out using a battery cycler (VERSASTAT3, Princeton Applied Research) at 25 °C. Partial pressures of evolving gases were periodically collected using a 6-way 2-position valve (EHLC6WM, VICI Valco Instruments) and analyzed using a mass spectrometer (RGA200, Stanford Research Systems) every 30 min.

*Preparation of seawater battery:* The carbon felts as a current collector of cathode were dried for 8 hours in an 80 °C vacuum oven. At the anode, sodium metal (1.54 cm<sup>2</sup>) was attached to a stainless steel spacer and 15  $\mu$ l of organic electrolyte was injected into a glove box under a high-purity Ar atmosphere. A 0.8 mm-thick NASICON-type solid electrolyte (Na<sub>3</sub>Zr<sub>2</sub>Si<sub>2</sub>PO<sub>12</sub>) and a seawater battery tester was purchased by 4TOONE Energy Co., Ltd. The assembled tester consists of Ni tap|anode|organic electrolyte|NASICON|salt water|carbon felt|Ti mesh. Natural seawater from Yeosu, Republic of Korea (GPS 34.773965, 127.747683) was used.

Sodium electrodes sampling for characterization: Galvanostatic cycled Na||Na symmetric cells were disassembled in the Ar-filled glovebox for sampling without air exposure. Then, sodium electrodes were washed several times to remove residual electrolytes on the surface, by using DME and PC, followed by vacuum drying in a glovebox antechamber for 10 minutes (DME for ether-based electrolytes, PC for carbonate-based electrolytes). Dried electrodes were transferred into the vial in a high-pressure glove box, followed by sealing with parafilm several times to prevent air penetration.

*SEM characterization:* Scanning electron microscope (SEM) was conducted using S-4800 (Hitachi) and Magellan400 (FEI Company). For sampling procedures, dried electrodes were loaded on the sample stage and then sealed in the vial. The sample stage was quickly loaded into the SEM chamber for minimizing the surface oxidation of sodium metal. The sample was observed with 10 kV acceleration voltage and 0.20 nA current of the electron beam.

*TOF-SIMS characterization:* TOF-SIMS was conducted using TOF.SIMS-5 (Ion-TOF) after sampling procedures. The Ar-filled plastic bag, instead of the glovebox, was used to minimize air exposure during sample transfer. TOF-SIMS measurements were conducted in the negative mode, and 3 keV, 20 nA or 30 nA of Cs<sup>+</sup> as a sputtering source to generate secondary ions. 30 keV, 0.6 pA of Bi<sup>3+</sup> ion beam was used for depth profiling. The sputtering and analysis area was 200  $\mu$ m × 200  $\mu$ m and 50  $\mu$ m × 50  $\mu$ m, respectively. The sputtering depths were estimated by SiO<sub>2</sub> sputtering depth under the same conditions.

*Electrolytes characterization:* The viscosity and ionic conductivity of the electrolytes were measured with a LVDV-ll+P viscometer (AMETEK Brookfield) and EUTECH CON 150 standard conductivity meter (Thermo Scientific) at 25.0 °C, respectively.

# 2. Figures



Fig. S1. Optical images of 1M NaBH<sub>4</sub>/glyme electrolytes



**Fig. S2.** Galvanostatic voltage profiles for Na||Na symmetric cells at 1 mA cm<sup>-2</sup> of current density and 1 mA h cm<sup>-2</sup> with different molar concentration of NaBH<sub>4</sub>/DEGDME. **a**) 0.5M, **b**) 1.3M, **c**) 1.36M

Note) The maximum concentration of NaBH<sub>4</sub> salt in DEGDME is 1.36M at room temperature. 0.5M NaBH<sub>4</sub>/DEGDME also delivers long-term cyclability of Na||Na symmetric cell, but the overpotential reaches 0.5V in the initial stage of cell operation, due to low concentration.<sup>2</sup>



Fig. S3. Galvanostatic voltage profiles for Na||Na symmetric cells at 0.5 mA cm<sup>-2</sup>, 1 mA h cm<sup>-2</sup>.
a) From the above, black) NaClO<sub>4</sub> EC/PC + 5 wt% FEC, red) NaOTf/TEGDME, blue)
NaBH<sub>4</sub>/DEGDME, green) NaBH<sub>4</sub>/TEGDME b) Converting time to cycle number at x-axis 90 ~ 110 cycles, c) 490 ~ 510 cycles.



Fig. S4. Galvanostatic voltage profiles of  $108 \sim 110$  cycle for Na||Na symmetric cells at 1 mA cm<sup>-2</sup>, 1 mA h cm<sup>-2</sup>. a) NaClO<sub>4</sub> EC/PC + 5 wt% FEC, b) NaOTf/TEGDME, c) NaBH<sub>4</sub>/DEGDME, d) NaBH<sub>4</sub>/TEGDME



**Fig. S5.** Galvanostatic voltage profiles of 508 ~ 510 cycle for Na||Na symmetric cells at 1 mA cm<sup>-2</sup>, 1 mA h cm<sup>-2</sup>. **a**) NaBH<sub>4</sub>/DEGDME, **b**) NaBH<sub>4</sub>/TEGDME



**Fig. S6.** Galvanostatic voltage profiles for Na||Na symmetric cells at 2 mA cm<sup>-2</sup>, 1 mA h cm<sup>-2</sup>. **a, b)** NaClO<sub>4</sub> EC/PC + 5 wt% FEC. **c, d)** NaOTf/TEGDME. **e, f)** NaBH<sub>4</sub>/DEGDME. **g, h)** NaBH<sub>4</sub>/TEGDME. **b, d, f, h** are enlargements of **a, c, e, g** respectively, for highlighting each result.



**Fig. S7.** Galvanostatic voltage profiles for Na||Na symmetric cells with intentionally punctured celgard separator at 1 mA cm<sup>-2</sup>, 1 mA h cm<sup>-2</sup>. **a**) NaBH<sub>4</sub>/DEGDME, **b**) NaBH<sub>4</sub>/TEGDME, **c**) Galvanostatic voltage profiles for Na||Na symmetric cells at 2 mA cm<sup>-2</sup> and 1 mA h cm<sup>-2</sup>.



**Fig. S8.** Measuring coulombic efficiency with modified Aurbach's measurement<sup>3</sup> in Na||Al half-cells, and digital photos of Al/C current collectors at position A and B in Fig. S8a. **a**) Galvanostatic voltage profiles of modified Aurbach's measurement in Na||Al half-cells. **b**, **c**, **d**, **e**) Digital photos for 5 mA h cm<sup>-2</sup> of sodium metal under 1 mA cm<sup>-2</sup> by applying NaClO<sub>4</sub> EC/PC+ 5 wt% FEC, NaOTf/TEGDME, NaBH<sub>4</sub>/DEGDME, NaBH<sub>4</sub>/TEGDME, respectively. (Position A in Fig. S8a) **f**, **g**, **h**, **i**) Fully stripping sodium metal on Al/C current collectors at 1 V cut-off voltage by applying NaClO<sub>4</sub> EC/PC + 5 wt% FEC, NaOTf/TEGDME, respectively (Position B in Fig. S8a).

Note) NaClO<sub>4</sub> EC/PC + 5 wt% FEC severely reacts with sodium metal, caused a short-circuit due to dendritic sodium growth during an initial high-capacity deposition process. As a result, no sudden voltage rise occurred during the first stripping process to the cut-off voltage of 1 V, and a very low overpotential of less than 5 mV was recorded during the intermediate cycle.



**Fig. S9.** EIS tests for Na||Na symmetric cells operated at 1 mA cm<sup>-2</sup>, 1 mA h cm<sup>-2</sup>. **a**) NaClO<sub>4</sub> EC/PC + 5 wt% FEC, **b**) NaOTf/TEGDME, **c**) NaBH<sub>4</sub>/DEGDME, **d**) NaBH<sub>4</sub>/TEGDME, **e**) NaClO<sub>4</sub> EC/PC + 5 wt% FEC 100 cycles, **f**) Equivalent circuit model for EIS tests

Note) NaClO<sub>4</sub> EC/PC + 5 wt% FEC appeared high SEI resistance ( $R_{SEI}$ ) around 60  $\Omega$ . As the cycle number was increased to 80 cycles,  $R_{SEI}$  continued to increase to 100  $\Omega$ , and even at 100 cycles, it sharply increased to 310  $\Omega$  with faulty profile at low frequency, which indicated the cell failure. In addition, the solution resistance (R<sub>s</sub>) of the electrolyte had the lowest value at every cycle among all electrolytes, owing to the highest sodium ion conductivity of 7.26 mS cm<sup>-1</sup> (Fig. S9a, S9e, and Table S2). In the case of NaOTf/TEGDME, total interfacial resistances  $(R_{tot} = R_{SEI} + R_{ct})$  at every 20th cycle were not escalated dramatically (~ 10  $\Omega$ ), which corresponds to a stable galvanostatic voltage profile (Fig. 1, Fig. S9b). Similarly, NaBH<sub>4</sub>/DEGDME did not appear a significant difference in interfacial resistance in 100 cycles (~ 6  $\Omega$ ), and it was much smaller than that of NaOTf/TEGDME. However, the R<sub>s</sub> of the electrolyte rises gradually with continuous cycling, which means the decrease of the ionic conductivity due to the reduction of electrolyte, forming the SEI layer (Fig. S9c).<sup>4</sup> Similarly, the R<sub>s</sub> of NaBH<sub>4</sub>/TEGDME also increased with continuous cycling. The gap between R<sub>tot</sub> rise moderately with increasing 20 cycles, and finally, it became negligible after 80 cycles (~  $40 \Omega$ ). These results are consistent with the voltage profile of NaBH<sub>4</sub>/TEGDME, which demonstrates an increase in overpotential up to the initial 100 cycles and stabilization thereafter (Fig. 1, Fig. S9d).



**Fig. S10.** SEM images and digital photos for Na||Na symmetric cells after 50cycles at 0.5 mA cm<sup>-2</sup>, 1 mA h cm<sup>-2</sup>. **a**, **b**, **c**) NaClO<sub>4</sub> EC/PC + 5 wt% FEC, **d**, **e**, **f**) NaOTf /TEGDME, **g**, **h**, **i**) NaBH<sub>4</sub>/DEGDME, **j**, **k**, **l**) NaBH<sub>4</sub>/TEGDME



**Fig. S11.** TOF-SIMS analysis for Na||Na symmetric cells after 50 cycles at 1 mA cm<sup>-2</sup>, 1 mA h cm<sup>-2</sup>. **a** ~ **d**) represents the surface of sodium metal anodes cycled by NaClO<sub>4</sub> EC/PC + 5 wt% FEC. **a**) Depth profile for Na<sub>2</sub><sup>-</sup> secondary ions, representative of dead sodium. **b**) Depth profiles for Cl<sup>-</sup> and F<sup>-</sup> secondary ions, representative of NaCl and NaF SEI layer. **c**) Depth profiles for C<sub>2</sub>H<sub>3</sub>O<sup>-</sup> and CHO<sub>2</sub><sup>-</sup> secondary ions, representative of organic SEI layers, originated from solvent decomposition. **d**) Depth profile for NaH<sup>-</sup> secondary ions, representative of NaH. **e** ~ **h**) 3D reconstructions of the TOF-SIMS signal, correspond to each secondary ion of depth profile results.



**Fig. S12.** TOF-SIMS analysis for Na||Na symmetric cells after 50 cycles at 1 mA cm<sup>-2</sup>, 1 mA h cm<sup>-2</sup>. **a** ~ **d**) represents the surface of sodium metal anodes cycled by NaOTf/TEGDME. **a**) Depth profile for Na<sub>2</sub><sup>-</sup> secondary ions, representative of dead sodium. **b**) Depth profiles for Cl<sup>-</sup> and F<sup>-</sup> secondary ions, representative of Na<sub>2</sub>S and NaF SEI layer. **c**) Depth profiles for C<sub>2</sub>H<sub>3</sub>O<sup>-</sup> and CHO<sub>2</sub><sup>-</sup> secondary ions, representative of organic SEI layers, originated from solvent decomposition. **d**) Depth profile for NaH<sup>-</sup> secondary ions, representative of NaH<sup>-</sup> secondary ion of depth profile results.



**Fig. S13.** Galvanostatic voltage profiles for Na||Na symmetric cells with artificial SEI layer of NaBO<sub>2</sub> or NaH under 2 mA cm<sup>-2</sup>, 1 mA h cm<sup>-2</sup>.



**Fig. S14.** OEMS analyses of two Na||Cu cells with 1 M NaBH<sub>4</sub>/TEGDME at the same conditions. **a**, **d**) Voltage profile of Na||Cu cells for initial 7~8 h rest and galvanostatic cycling at 0.5 mA cm<sup>-2</sup> and 1 mAh cm<sup>-2</sup>. **b**, **e**) Partial pressures of detecting gases during cell operations. **c**, **f**) Highlighting H<sub>2</sub> partial pressure in **b**) and **e**), respectively.

Note 1) Due to high volatility, DEGDME solvent could not be used for OEMS analysis. We used TEGDME as the same family of the glyme solvent. We also confirmed similar SEI layers formed from DEGDME and TEGDME in **Fig. 3**.

Note 2) A sharp bump evolving  $H_2$  gas appeared at the very initial cell operation. It was presumably attributed to the electrochemical reduction of the native oxide layer over a mesh-type Cu foam (CuO, Cu<sub>2</sub>O, and Cu(OH)<sub>2</sub>).<sup>5</sup> Similar  $H_2$  bumps emerged for two cells (**Fig. S14c**) and **f**)), while there was a negligible signal for the O<sub>2</sub> and CO<sub>2</sub> cases at the same operating period (**Fig. S14b**) and **e**)). These results excluded the possibility that the  $H_2$  bump was artificial noise.



Fig. S15. Na 1s XPS of metallic sodium.

Note) Fig. S15 demonstrated the native oxide layer on sodium even in highly restricted glovebox. In Fig. S15, shiny, metallic sodium was prepared in an Ar-filled glovebox and then hermetically sealed in a glass bottle ( $O_2 < 0.1$  ppm,  $H_2O < 0.1$  ppm). Similarly, sample transfer and analysis were performed on XPS connected to Ar-filed glovebox ( $O_2 < 0.5$  ppm,  $H_2O < 0.1$  ppm). As a result, we suggest two possibilities; 1) trace amount of oxygen and moisture in glove box (under detection limit of sensor) 2) Oxygen adsorbed on materials in glovebox, such as labwipers. In addition, a small amount of oxygen present in the electrolyte can also oxidize the sodium metal apart from Fig. S15.



**Fig. S16.** 3D reconstruction images obtained from TOF-SIMS results of bare Na metal cube surface, corresponding to Fig. 4a.  $\mathbf{a} \sim \mathbf{c}$ ) 3D reconstruction images for Na<sub>2</sub><sup>-</sup>, NaO<sup>-</sup>, and NaOH<sup>-</sup> represent sodium metal, native oxide layer, and NaOH, respectively.



Fig. S17. 3D reconstruction images obtained from TOF-SIMS results of bare Na metal cube surface, corresponding to Fig. 4d.  $a \sim e$ ) 3D reconstruction images for Na<sub>2</sub><sup>-</sup>, NaO<sup>-</sup>, NaOH<sup>-</sup>, NaH<sup>-</sup>, and BO<sub>2</sub><sup>-</sup> represent sodium metal, native oxide layer, NaOH, NaH, and NaBO<sub>2</sub> SEI layer, respectively.

Note) In **Fig. 4**, the intensity of each secondary ion was normalized by total counts for alleviating matrix effect and surface roughness, while, the 3D reconstruction images are not able to reflect the normalization due to the limit of software. Because the total count of bare Na is much higher than treated Na, the 3D reconstruction results of treated Na show lower intensity than bare Na. Fig. S11, S12 deliver the visualization of the "SEI layer reconstruction" by NaBH<sub>4</sub>/glyme electrolytes by proving the change of existing chemical species.



**Fig. S18.** Galvanostatic voltage profiles for bare Na and treated Na at 2 mA cm<sup>-2</sup> and 1 mA h cm<sup>-2</sup> by using NaOTf/TEGDME electrolyte.



Fig. S19. Photograph of seawater flow cell tester.



**Fig. S20**. EIS tests for sea water battery full cell before and after cycling under 1 mA cm<sup>-2</sup>, 1 mA h cm<sup>-2</sup>. **a)** NaBH<sub>4</sub>/DEGDME, **b)** NaBH<sub>4</sub>/TEGDME



**Fig. S21.** Charge-discharge curves for seawater battery by using NaOTf/DEGDME at 1 mA cm<sup>-2</sup>, 1 mA h cm<sup>-2</sup>.



**Fig. S22.** SEM images for seawater battery after operating 10 hours at 1 mA cm<sup>-2</sup>, 1 mA h cm<sup>-2</sup>. **a, b**) NaOTf/TEGDME **c, d**) NaBH<sub>4</sub>/DEGDME, **e, f**) NaBH<sub>4</sub>/TEGDME

![](_page_26_Figure_0.jpeg)

**Fig. S23.** XRD patterns of pristine NASICON, NASICON immersed in NaBH<sub>4</sub>/DEGDME for 24 h, and reference.

![](_page_27_Picture_0.jpeg)

**Fig. S24. a)** Photographs of pristine NASICON and **b)** NAISCON immersed in NaBH<sub>4</sub>/ DEGDME for 24 hours. No dicernible change was observed.

![](_page_28_Figure_0.jpeg)

Fig. S25. Radar plot evaluating the F-based reference electrolytes and developed electrolytes

![](_page_29_Figure_0.jpeg)

**Fig. S26.** Cycling performances of bare Na and treated Na in Na||Na<sub>0.83</sub>Fe<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> full-cell at 1C-rate. **a**) Long-term cyclability **b**) 1<sup>st</sup> cycle, **c**) 50<sup>th</sup> cycle, **d**) 100<sup>th</sup> cycle of discharge curve.

Note) Bare Na-based cell recorded lower capacity retention (47.30%) than treated Na-based cell (50.48%, Fig. S26a). In particular, a difference between bare Na and treated Na in the first cycle of a discharge curve is negligible (Fig. S26b), but the overpotential increase in untreated Na-based cell is larger than in treated Na cell (Fig. S26c, d). The preformed NaH-based SEI layer contributed to improving cyclability of the sodium metal anode because severe side reaction of the electrolyte (1M NaClO<sub>4</sub> EC/PC + 5 wt% FEC) was mitigated by the NaH-based SEI layer produced by "SEI reconstruction."

### 3. Tables

	Cost	Molecular weight	Salt cost	Purity
	[\$ g <sup>-1</sup> ]	[g mol <sup>-1</sup> ]	[\$ per 10 ml electrolyte]	[%]
NaClO <sub>4</sub>	0.76	122.44	0.93	98
FEC	47.06	106.05	32.53	> 99%
NaOTf	20.29	172.06	34.91	98
NaPF <sub>6</sub>	4.06	167.95	6.82	98
NaBH <sub>4</sub>	0.78	37.83	0.30	98
NaBH <sub>4</sub>	1.72	37.83	0.65	99
NaBH <sub>4</sub>	5.74	37.83	2.17	99.99

Table S1. Cost-effectiveness of NaBH4 salts compare to typical sodium salts

Note) The cost of each electrolyte salt was searched in Sigma-Aldrich

	Viscosity	Ionic conductivity
	[cP]	[mS cm <sup>-1</sup> ]
NaClO <sub>4</sub> EC/PC 5wt% FEC	6.26	7.26
NaOTf/TEGDME	8.56	1.28
NaBH <sub>4</sub> /DEGDME	2.13	0.94
NaBH <sub>4</sub> /TEGDME	7.99	0.51

 Table S2. Basic properties of 1M concentration electrolytes

Т	$\Delta \mathbf{H}$	$\Delta \mathbf{S}$	$\Delta \mathbf{G}$
[K]	[kJ mol <sup>-1</sup> ]	[J mol <sup>-1</sup> K <sup>-1</sup> ]	[kJ mol <sup>-1</sup> ]
0	-52.021	0	-52.021
298.15	-56.442	-76.777	-33.551
300	-56.454	-76.820	-33.408

**Table S3.** Thermodynamic parameters of the Na(crystal) +  $1/2H_2 = NaH(crystal)^6$ 

Electrolyte	Current density [mA cm <sup>-2</sup> ]	Capacity [mA h cm <sup>-2</sup> ]	Cycle life [h]	Reference
5M NaFSI/DME	0.0028	0.0014	600	7
0.1M NaBPh <sub>4</sub> /DME	0.5	0.5	600	8
2.1M NaFSI	1	1	950	9
DME/BTFE (1:2)				
1M NaDFOB	1	1	115	10
EC/DMC (1:1)	1	1		
1M NaPF6	1	1	550	11
FEC/PC/HFE + PFMP	1	1	550	11
1M NaPF <sub>6</sub>	1	1	800	12
DME/FEC/HFPM				
1M NaPF <sub>6</sub> /glyme				
(DME, DEGDME,	1	1	600	13
TEGDME)				
1.0 M NaClO <sub>4</sub> EC/PC	0.5	1	500	14
+ 50 mM SnCl <sub>2</sub>	0.0			
1M NaPF <sub>6</sub> /DEGDME	2	1	400	15
$+ 0.033 \text{ M Na}_2\text{S}_6$	~			
1M NaBH <sub>4</sub> /glyme (DEGDME, TEGDME)	1	1	1200	This work

Table S4. A summary of the published work on electrolytes for sodium metal anodes

Electrolyte	Current density [mA cm <sup>-2</sup> ]	Cycle life [cycle number]	Reference	
1M Na-biphenyl				
+ 0.7M Na-pyrene	0.5	50	16	
+ 0.5M NaPF <sub>6</sub> /DEGDME				
1M Na-	0.5	80	17	
biphenyl/DEGDME	0.5	80	1 /	
3M Na-biphenyl/DME	1	100	18	
1M NaClO <sub>4</sub> /EC/PC	0.05	30	19	
1M NaOTf/TEGDME	0.05	100	19	
Ionic liquid electrolye	0.05	50	20	
(Pyr <sub>14</sub> TFSI)	0.05	50	20	
1M NaBH <sub>4</sub> /DEGDME	1	150	This work	

 Table S5. A summary of the published work on electrolytes for seawater batteries

#### 4. Supplementary notes

#### Supplementary note 1) Superiorities of NaBH\_/DEGDME than F-based electrolyte

#### 1. Superior electrochemical performance

The NaBH<sub>4</sub>/DEGDME electrolyte not only showed better electrochemical performance than the F-based reference electrolyte in symmetric cells (Fig. 1, S3, S6), but also in half-cell (Fig. S8) and practical SWBs (Fig. 5). Especially, it delivers higher coulombic efficiency, better SWBs compatibility, and rate capability than NaOTf/TEGDME, which are commonly used in various next-generation battery systems (Na-air, Na-CO<sub>2</sub>, SWBs).

#### 2. Outstanding cost-effectiveness

As we mentioned in the manuscript, NaBH<sub>4</sub> is the most cost-effective material, even at high purity (99.99%). In addition, it has a low molecular weight (37.83 g mol<sup>-1</sup>), which implies that low-mass NaBH<sub>4</sub> salt is needed to produce the same concentration of electrolytes as other salts (\$2.17 for 10 ml, 1M NaBH<sub>4</sub>/glyme, Table S1, ESI†). In particular, NaOTf costs approximately 17 times when producing the same volume of electrolytes, despite its much lower purity. As a result, NaBH<sub>4</sub> is economically feasible and practical, as well as outperforming the NaOTf/TEGDME used in conventional SWBs

#### 3. Eco-friendly and harmless of NaBH<sub>4</sub>

Fluorine is a highly essential element in the electrolyte, but it is known to be harmful to the nature and the human body because of its toxicity<sup>21, 22</sup>. The disposal of waste batteries have recently become a social challenge, and the use of F-based electrolytes exacerbates the issue.<sup>23</sup> In particular, the  $PF_6^-$ , which is widely used in lithium and sodium-based batteries, is widely known to produce HF by hydrolysis. Since HF is strictly restricted from exposure and disposal and has a significant adverse effect on the human body and the environment, the use of  $PF_6^-$  should be reduced. On the other hand, when NaBH<sub>4</sub> is exposed to moisture during disposal, NaBO<sub>2</sub> and H<sub>2</sub> are produced, neither of these compounds is harmful to the environment or human health.

#### Supplementary note 2) Operating mechanisms of seawater batteries

The cathode of a seawater battery (SWB) employing seawater containing Na<sup>+</sup> and Cl<sup>-</sup> ions can be charged and discharged through the sodiation/desodiation reaction at the anode and evolution/reduction of O<sub>2</sub> and Cl<sub>2</sub> at the cathode. The Pourbaix diagram of water including Cl<sup>-</sup> ions shows that the oxygen evolution/reduction reaction (OER/ORR) is thermodynamically favored over the chlorine evolution/reduction reaction (CIER/CIRR).<sup>24</sup> In seawater condition (Na ion concentration: 0.47 M, pH: 8, oxygen partial pressure: 100 % saturation), the reaction mechanism and the theoretical voltage are as follows:

Anode: 
$$Na^+ + e^- \leftrightarrow Na; E^0 \approx -2.73 V vs. NHE$$
  
Cathode:  $O_2 + H_2O + 4e^- \leftrightarrow 4OH^-; E^0 \approx 0.75 V vs. NHE$ 

Overall:  $4Na(s) + 2H_2 + O_2 \leftrightarrow 4NaOH(aq); E \approx 3.48 V$ 

During charging, energy can be stored by the OER at the cathode and the sodiation reaction at the anode and Na<sup>+</sup> ions are transported from seawater to anode part through NASICON. During discharging, electricity can be produced by the ORR at the cathode and the desodiation reaction at the anode.

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